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Investigation of the potential release of polychlorinated dioxins and furans from PCP-treated utility poles

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Abstract

The United States (US) Environmental Protection Agency (EPA) estimated that the use of technical grade pentachlorophenol (PCP) between 1970 and 1995 to treat wood was approximately 400 000 metric tons in the US, and that between 4800 and 36 000 g of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalents (TEQs) were incorporated annually in treated wood. The EPA has been unable, however, to estimate the rate of release of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (CDD/Fs) from treated utility poles into the environment. There is some evidence that CDD/Fs leach from treated poles into the surrounding soils, but these studies do not allow for the calculation of a rate of release from this mechanism. Another possible release mechanism is the volatilization of dioxins into the atmosphere, but there are no data to demonstrate, much less quantify, this release. While not directly measuring the release of dioxins from treated utility poles into the environment, this study was designed to examine the potential for such release. The general approach taken was to collect PCP-treated poles of varying ages, to remove and analyze multiple samples from each pole cross-section, and to compare the spatial distribution of CDD/F congeners among poles of different ages. Evidence of concentration–depth profile changes over time may provide insight into the potential for dioxins to migrate through and then out of PCP-treated utility poles. It was found that the CDD/F concentrations were consistently higher in the outer portions of the poles than the center. This trend tends to be most marked in older poles and for the lower chlorinated congeners. The trend for dioxins to concentrate in the outer portions of the pole over time suggest migration within the poles, and this migration may result in some environmental release. Other possible explanations were also offered.

Keywords: Dioxins; Furans; Pentachlorophenol

1. Introduction

Technical grade pentachlorophenol (PCP) has been used as a preservative in utility poles in the United States (US) and Canada since 1941 (Leutritz, 1971). It has been estimated that 400 000 metric tons of PCP were used during the period from 1970 to 1995 in the US (EPA, 2000a). PCP is known to contain polychlorinated dibenzo-*p*-dioxins and dibenzofurans (subsequently referred

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to as dioxin-like compounds, dioxins and furans, or CDD/Fs). The levels have varied over time as manufacturing methods have changed. Following implementation of regulations in 1987, monthly measurements of CDD/F congener group concentrations in technical grade PCP used in the US have been reported (EPA, 1999). These data suggest a decline in dioxin and furan concentrations in PCPs from the mid/late 1980s to the mid/late 1990s. While these data on congener group concentrations are available, more detailed analyses in which congener-specific values are obtained are not generally available. The limited data on congener-specific concentrations of CDD/Fs in PCP have allowed for calculations of toxically equivalent (TEQ) concentrations, and these have ranged from approximately 1.7 mg TEQ/kg PCP during the late 1980s to approximately 0.6 mg TEQ/kg PCP in formulations into the 1990s (EPA, 2000a). [Calculations of 'TEQ' use the World Health Organization's Toxicity Equivalency Factor Scheme (Van den Berg et al., 1998) for calculating TEQ concentrations and quantities, unless otherwise specified.]

There have been limited efforts to study the movement of PCP and CDD/Fs from treated poles into the environment. Ruddick (1991) hypothesized that depletion of PCP in treated utility poles was controlled by five basic mechanisms: movement of carrier oil; evaporation; water leaching; photochemical decomposition; and biological degradation. This analysis may be extended to CDD/F. Of the possible depletion mechanisms, water leaching and evaporation would result in the transfer of CDD/F to the environment. There is some evidence that CDD/F leaches from treated poles into nearby soil (Gurprasad et al., 1995; EPRI, 1995). However, these studies do not provide sufficient information to estimate a release rate of this mechanism.

Some rough estimates of CDD/F release from treated wood have been made. Bremmer (1994) estimated an annual release of 15–125 g I-TEQ from PCP-treated wood in the Netherlands based on estimates of CDD/F concentrations in PCP and an assumed range of half-lives of CDD/F in treated wood of 15–150 years [TEQs calculated using the International Scheme (EPA, 1989), abbreviated I-TEQ]. Rappe (1995) used the emission factor approach developed by Bremmer and assumed that 0.5 million metric tons of PCP were used in the US over the past 50 years to estimate that 10.5 kg I-TEQ could potentially volatilize from PCP-treated wood annually. Eitzer and Hites (1987) estimated that 3 kg I-TEQ per year were released from the poles. They based their estimate on the assumption that 0.1% of the PCP produced annually enters the atmosphere and the CDD/F contained in the PCP (assumed to be 130 mg I-TEQ/kg PCP) are released at the same rate.

These releases are compared to the EPA's estimates of total emissions in the US from all quantified sources (e.g. waste incinerators) to be 12 kg TEQ in 1987 and 3 kg TEQ in 1995 (EPA, 2000a). PCP-treated wood was characterized as a 'reservoir source' in EPA (2000a). Reservoirs were defined as materials or places that contain previously formed CDD/Fs and have the potential for redistribution and circulation of these compounds into the environment. The most extensive reservoir source is soil. Sediments and vegetation also qualify as reservoir sources based on this definition. EPA (2000a) concluded that existing data were insufficient to support a reasonable estimate of the releases of CDD/Fs from the reservoir of PCP-treated wood.

The size of the dioxin reservoir in poles and the fact even low release rates have the potential for significant environmental releases highlight the need for more rigorous examination of the emission of CDD/F from PCP-treated utility poles. One potential approach to conducting this examination would be to measure the CDD/F content of a large number of poles with a variety of service times. By examining the CDD/F concentrations as a function of depth into the pole, it may be possible to observe a systematic change in the concentration–depth profile over time, and from that, to model the release of CDD/Fs from poles as a function of time in service. However, given the large effort that would be entailed in such a program, the EPA initiated a pilot project to determine if the approach had the potential to

Table 1
Poles analyzed in 1997, 1998 and 2000

Treatment date	Date sampled	Length of service at time of sampling, years
1963	2/97	34
1973	1/97	24
1987	5/98	11
1987	6/98	11
1994	5/98	4
1994	8/00	Repeat analysis of 1994 pole after 2 years of storage
1996	2/97	0
1997	6/98	1
1999	8/00	0
Untreated	1/97	Not applicable

produce useful results. This pilot study was designed to meet these objectives: (1) develop a reliable method for measuring spatial distributions of dioxin in treated poles; (2) determine if a measurable change in CDD/F concentration occurs over time; and (3) provide information from which the need for and design of a more exhaustive study can be assessed.

2. Methods

This project was performed over a 4-year period in which the poles with service periods ranging from 1 to 34 years were collected, sampled, and analyzed. The methods were designed to accommodate the wide range in pole conditions.

3. Sampling

3.1. Selection criteria

Poles were selected for inclusion in the study based on several criteria. First, they had to have a legible brand indicating that they were PCP-treated and that the treatment date was appropriate. It was desired to have poles representing a variety of service lengths. There were no efforts to insure that sampled poles were from a similar treatment lot or were of a similar wood type — the emphasis was on verifying PCP treatment and treatment date. During a first round of pole sampling in 1997, poles of long service length were sought, and eligible poles of 24 and 34 years of service length were found. Also, a freshly treated and an untreated control pole were sampled during this first round. The second round in 1998 focused on poles of more recent service length, and poles of 1, 4 and 11 (2 poles) years were sampled. The 11-year-old poles were from different lots and therefore may have been treated with PCP differently, and may be comprised of different wood types. The purpose of selecting two poles of the same age was to conduct tests of replicability; i.e. whether poles of the same age would have similar results (see discussion below). A third round in 2000 included a second freshly treated pole and a resampling of the 4-year-old pole, a portion of which remained in storage. In addition, the prospective sample poles needed to be intact and free from significant cracks that may interfere with data analysis. Over 200 utility poles were investigated for possible sampling. In most cases, poles were excluded based on a lack of a legible brand, or brand information indicating that the pole was treated on a non-target date. Table 1 summarizes the pole sampling program.

3.2. Sample acquisition

A 3-foot section was removed from each selected pole. The sections collected were taken from portions of the poles that were at least 8 feet above the ground line to minimize the impact of potential ground level contamination sources. Prior to cut-

ting, the north side of each pole was marked and photographs of each side of the pole were taken.

Once a section was removed from the pole, the ends of the section were examined to determine if the growth center of the tree from which the pole was manufactured and the geometric center of the pole were close together. Any pole in which the two centers differed by more than 10% of the radial distance at either end of the section was discarded. This check was performed to minimize the impact of the difference in the permeability of the heartwood and the sapwood on the final results.

One of two approaches was used to extract samples from each of the collected pole sections. These methods are described below. Method 1 was used for the sections collected during the first project year (the untreated pole, one of two freshly treated poles, and the poles with service periods of 24 and 34 years). Method 2 was used for the remainder of the samples (the second freshly treated pole, the two poles with 11-year service periods, the pole with a 4-year service period, the second analysis of this 4-year service pole, and a 1-year service pole).

3.2.1. Method 1

Each end of the section was first removed using a band saw to ensure that any contamination from the lubricating oil used in the chain saws used to cut the section from the pole was eliminated. The blade of the band saw was cleaned prior to use and wipe tested to ensure that it was free of contamination. The pole section was then cut into three equal lengths. The center section was archived while the two end sections were further divided into 5-cm (2 inches) slabs. The top of each slab was marked with the pole number and slice number using a carpenter's pencil. The slab was brushed to remove any adhering sawdust and then placed in a plastic bag. The bag was marked with the slab's identification number and the top of the slab was indicated. Chalk and pencil markings on the pieces sometimes faded. The oil in the freshly treated pole sections, in particular, tended to absorb chalk markings.

The slabs were then transported to the sampling location. A drill press equipped with a 0.95-cm (3/8 inch) spade drill bit was used to produce wood shavings from a given location. The samples

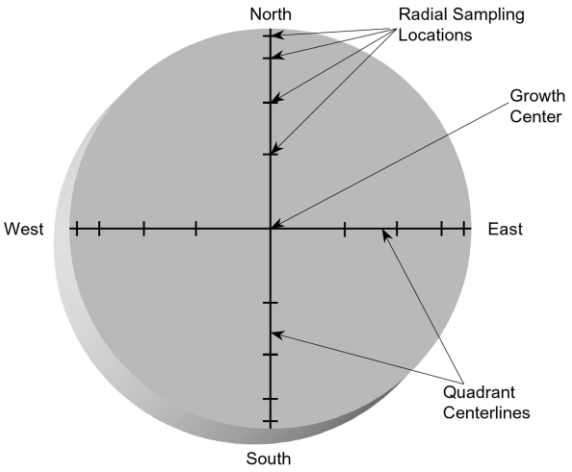

Fig. 1. Sampling locations used.

were made up of the wood shavings generated during the drilling process. To define the locations on each slab from which samples were obtained, the center lines of quadrants were marked on the top of each slab as shown in Fig. 1. For slabs obtained from the upper portion, the north and south locations within the north and south quadrants of the pole were used to obtain wood shavings for analysis. For the lower portion, the east and west quadrants were used. Next the radial sampling locations were marked along each quadrant centerline. The radial locations were at the following distances from the growth center of the pole (where '*r*' represents the radius of the pole measured along the quadrant centerline being used): 0 (pole center); 0.354 *r*; 0.612 *r*; 0.790 *r*; and 0.936 *r*. The average radius of the poles used was 12 cm (4.6 inches). Thus, the average sampling locations corresponded to 0.8, 2.5, 4.7, 7.8 and 12 cm from the surface of the pole (0.3, 1.0, 1.8, 3.0 and 4.6 inches).

A series of small holes was created at each radial position using the 0.95-cm (3/8 inch) spade bit on a variable-speed drill press. The location of these holes is shown in the photograph of one of the sample slabs in Fig. 2. A new drill bit, cleaned with reagent grade acetone, was used for each pole piece. Samples from older poles exhibited significant cracking, which could cause the slab to fall apart during sampling. Thus, the slabs generated from these poles were held together with large

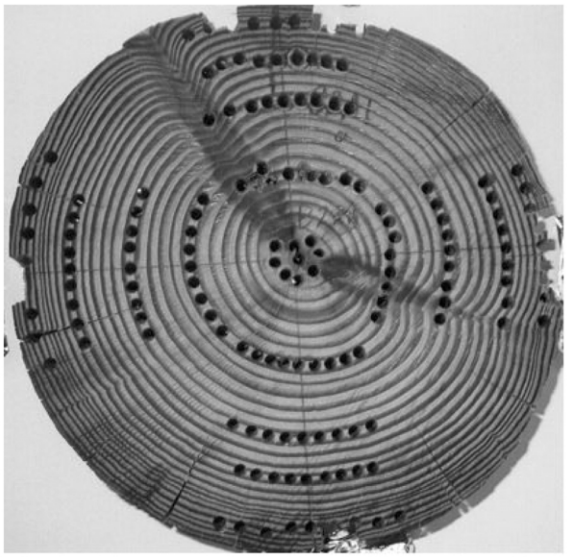

Fig. 2. Photograph showing example pattern of holes in pole sampling.

band clamps. All of the wood shavings obtained from the same radial location in each slab created from the portion of the pole section were combined to form a single sample.

After each set of holes was drilled, the slab was carefully brushed off and the holes plugged. After a complete sample was obtained, the end 3 mm (1/8 inch) was cut off of the brush's bristles to prevent cross-contamination. The samples of wood shavings were placed in 9-oz wide-mouthed sample jars with Teflon lids, which were purchased pre-cleaned for metals and organic compounds. Each sample was labeled with its unique sample identification number and transferred to the laboratory for analysis. Each sample weighed approximately 24 g.

3.2.2. Method 2

In this sampling method, the ends of the pole section were first removed as in the previous method. However, the section was then divided into three unequal pieces. The upper portion was 41 cm (16 inches) long, the middle portion was 10 cm (4 inches) long, and the bottom piece was 41 cm (16 inches) long. The top piece was used to generate the samples used for the CDD/F determination, the middle was used for the PCP determination and the bottom portion was archived.

The top 41-cm (16 inches) section was cut into eight slabs 5 cm (2 inches) thick, and the top of each slab was marked with the pole number and slice number using white chalk or a pencil. The 'North' direction had already been marked on the side of each slab. Any adhering sawdust was removed before placing slices in zip-lock bags. The top of each slice was marked into four quarters and four arcs centered on the growth center as in Method 1.

4. Analytical methods and quality control

The sample preparation and analysis procedure used was a laboratory specific adaptation of EPA Methods 8290, 1613B and 1668. The 17 2,3,7,8-substituted dibenzo-*p*-dioxin and dibenzofuran (CDD/F) congeners shown in Table 2 were determined using an isotope dilution method (EPA

Table 2
CDD/F congeners measured in utility poles

Dioxins	Furans
2,3,7,8-Tetrachlorodibenzodioxin (TCDD)	2,3,7,8-Tetrachlorodibenzofuran (TCDF)
1,2,3,7,8-Pentachlorodibenzodioxin (PeCDD)	1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)
	2,3,4,7,8-PeCDF
1,2,3,4,7,8-Hexachlorodibenzodioxin (HxCDD)	1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDF
	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-Heptachlorodibenzodioxin (HpCDD)	1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)
	1,2,3,4,7,8,9-HpCDF
Octachlorodibenzodioxin (OCDD)	Octachlorodibenzofuran (OCDF)

Method 1613B). The sediment procedure was used for extraction of the sawdust samples. A Dean-Stark trap was placed on top of a Soxhlet extractor to collect moisture from the wood matrix. Each matrix was fortified with ^{13}C-labeled CDD/F congeners and extracted with toluene. Sawdust (10 g) (on a dry weight basis) was used in each extraction. Before cleanup of the extract, the solvent was exchanged to hexane and fortified with ^{37}Cl-labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The extract was sequentially partitioned against concentrated acid solutions and then eluted through an acid silica gel column, neutral alumina column, and Carbopack C/Celite 545® carbon column. The final extract was fortified with two 13 C-labeled dioxins and adjusted to a final 10 μl in tridecane or nonane. The extracts were analyzed using High-Resolution Gas Chromatography with a High-Resolution Mass Spectrometer detector (HRGC/HRMS).

Before use, all glassware in the preparation laboratory was inspected for cracks and chips. All glassware was carefully cleaned. Method blank results were used to verify that proper glassware cleaning procedures were used in the study. Burdick and Jackson distilled-in-glass solvents were used in all rinsing and sample preparations. Solvents were analyzed for CDD/F before use. Reagent water was obtained from an 18 MΩ Milli-Q water system.

Two methods were used to determine PCP concentrations. For the samples collected in the first year of the study (from the 34-year-old, 24-year-old, one of the freshly treated, and the untreated pole), Gas Chromatography using an Electron Capture Detector (GC/ECD) was used. Several dilutions were required for analysis as concentrations were very high in the treated wood. Given these high concentrations, and with other objectives to conserve costs and focus on dioxin and furan analysis, a commercially available enzyme-linked immunosorbent assay (ELISA; made by Millipore and called the EnviroGuard®) method was used to determine PCP concentrations and profiles in later stages of the study. This analysis was performed in a manner similar to EPA SW-846 Method 4010 (EPA, 1996). Measurements were based on competitive binding between PCP extracted from samples with a PCP-enzyme conjugate in antibody-coated tubes. A color reagent was added to each of the tubes, which reacts with the bound PCP-enzyme conjugate to generate a blue color. Addition of hydrochloric acid produced a final yellow color that was monitored using a spectrophotometer set at a wavelength of 450 nm. This method has been adapted from a commercially available field-compatible test for screening soil samples.

Prior to study initiation, method development was conducted to verify the methods for analyzing CDD/Fs in wood. Method development included first measuring the CDD/F congeners in an untreated pole, and then spiking other samples of the untreated pole at low and medium levels of the congeners. Lower chlorinated dioxins were largely undetected in the untreated sample, while higher chlorinated congeners were found at 10s to 100s of parts per trillion, levels a bit higher than expected for vegetation (see Results 1. Concentrations below for discussion), but at levels judged sufficient to begin analysis. Four replicates per spiking treatment were analyzed. Method precision overall was very good and it was judged that differences observed in treated pole results could likely be distinguished from any variations in method performance. The absolute recoveries of the $^{13}C_{12}$ internal quantitation standards were well within the objective of 25–150%. Specifically, for over 300 analyses (18 congeners, 17 samples including method blank recoveries) of the method development stage, the recoveries ranged from 45.5 to 116% with a mean of 75.2% and a R.S.D. of 10.7%.

QA/QC during both rounds of analysis of study samples, in 1998 and 2000, included method blanks, ongoing precision and accuracy matrix spikes, and duplicate matrix spikes. For both rounds, QA/QC results were again judged very reasonable, with spike recoveries in the range of 59.7–120%, with an overall study mean of 91.5%, and a R.S.D. of 10.6%.

Another QA/AC test performed during both rounds of study was to analyze duplicate samples of study poles without spiking. It is expected that

duplicates of study samples should have very similar results. An appropriate measure of the variability from this duplicate study sample QA/QC test can be used to describe the variability that is due to analytical chemistry alone. This will prove useful in evaluating results from specific pole samples taken to study the issue of 'replicability': how 'similar' or 'equal' are two distinct PCP-treated poles? Three pairs of study poles were used to examine this issue of replicability. These three pairs included: two freshly treated poles which were treated during different years (could all freshly treated poles be considered 'equal'?); two 11-year-old poles which had different treatments (could poles of the same age but of possible different wood types and treatments be considered 'equal'?); and two samples from the same 4-year-old pole, but from different locations and the second set analyzed 2 years later in time (does pole location and time in storage affect pole results?).

During the first round of sampling, six duplicate samples from two poles (three samples each) were analyzed for 10 CDD/F congeners, including two tetra congeners, three penta, three hepta, and two octa congeners. During the second round, two duplicate samples from two poles (one sample each) were analyzed for seventeen CDD/F congeners. The concentrations ranged from the low parts per trillion (ppt) for the tetra congeners to >4.0E6 ppt (4 ppm) for the octa congeners. While it is clear that the methods were capable of identifying this extremely wide range in results, it is more important here to know how well duplicate samples matched each other. For that purpose, a 'relative percent difference', RPD, measure was used. This is defined as: $[(\text{high}-\text{low})/\text{average}]\times 100\%$, where 'high' is the higher of the two measurements, whichever it was.

RPD QA/QC results for both rounds of sampling are shown in Table 3. All individual congener results are aggregated according to degree of chlorination (see Section 5.1). Shown there are average concentrations found in the samples, the average RPD for each aggregated set of pairs, and the standard deviation of the RPD for each aggregation. Generally, the smaller the RPD and the smaller the standard deviation of the RPDs, the better the analyses are 'duplicated'. As seen, there was a difference in the performance in the two rounds. The RPDs of the first round ranged from 37 to 50%, with an average of 46, with standard deviations around these RPDs similarly ranging from 30 to 59, with an average of 46. For the second round, the analytical performance improved significantly, with RPDs dropping to a range of 13–34%, with an average of 21%, and the S.D. around these RPDs ranging from 7 to 42, with an average of 29. These RPDs will be used when evaluating replicability in the results section below.

Table 3
Concentrations found (ppt, dry weight) and relative percent differences (RPDs, %) found in duplicate analyses of study samples during two rounds of study

Description	Number of pairs	Mean concentration, ppt	RPD, %	S.D. of RPD
I. First round of study, 1998				
Tetra	3	45	37	30
Penta	12	394	50	59
Hexa	NA	–	–	–
Hepta	6	253 000	42	35
Octa	10	1 812 000	44	37
Overall	31	–	46	43
II. Second round of study, 2000				
Tetra	NA	–	–	–
Penta	6	58	13	7
Hexa	12	4000	23	42
Hepta	6	196 000	18	14
Octa	4	2 235 000	34	23
Overall	28	–	21	29

NA, results not available due to non-detected or not analyzed.

Moisture analysis and wood density were performed gravimetrically. Drying in a temperature-controlled oven (110 °C) was used to determine moisture content of each sample.

5. Results

Eight poles, with lengths of service of 0 (2 poles), 1, 4, 11 (2 poles), 24 and 34 years, were sampled at the center and four radial locations in each of four quadrants for a total of 17 samples per pole. To maximize the efficiency and minimize the cost of the program, selected samples were not analyzed, so that less than 17 samples were analyzed per pole (8 poles×17 samples=136 sam-

ples; a total of 106 samples were taken). However, at least two samples from each radial distance in each pole were extracted and analyzed. In the early stages of the program, an interferant degraded the results for the hexachlorinated congeners. Thus, no acceptable data for these congeners are available for the freshly treated, 24 and 34-year-old poles. An interferant also degraded the results for one of the fresh poles for one of the pentachlorinated furans. Interepretive analysis was avoided for compounds for which no data were available due to interferants. PCP analyses were not performed on the 1, 4 and 11-year-old poles. From these eight poles, there was a resulting total of 1484 concentration measurements (for 10 congeners and 4 aggregate group totals = 14) from 106 samples ($106 \times 14 = 1484$). Table 1 summarizes all 10 poles of this sampling program.

For some of the interpretive analyses performed below, concentration results were aggregated. As a way of normalizing the results for each pole, so that trends from all poles could be compared, 'concentration ratios' were determined. These are equal to the ratio of a specific pole concentration and the average pole concentration. Contour plots were also generated to describe how the concentrations varied for each pole cross-section. Procedures for aggregation, normalization, and contour plot generation are now presented.

5.1. Aggregation

For some of the analyses, the data were aggregated by summing the concentrations for each dioxin and furan congener that has the same degree of chlorination. This was done for purposes of simplifying the interpretation of the data. Its validity is based on the assumption that dioxin and furan congeners with the same degree of chlorination would have roughly the same sorptive tendencies on the wood. EPA (2000b) report on the fate properties of the dioxin-like compounds, and they reported lower log Kow for lower chlorinated congeners and higher log Kow for the higher chlorinated congeners. Specifically, the log Kow for 2,3,7,8-TCDD and 2,3,7,8-TCDF was 6.8 and 6.1, respectively. The log Kow for all penta congeners similarly ranged from 6.4 to 6.8; for the hexa congeners, there was less mobility with a range of 7.0–7.8, a similar range of 7.4–8.0 for the hepta congeners, and the log Kow for OCDD and OCDF were 8.2 and 8.0, respectively. Thus, the following aggregate groups were obtained:

- ***TCDD/F*** which consisted of the sum of 2,3,7,8-TCDD and 2,3,7,8-TCDF;
- ***PeCDD/F*** which consisted of the sum of 1,2,3,7,8-PCDD; 1,2,3,7,8-PCDF, and 2,3,4,7,8-PCDF;
- ***HxCDD/F*** which consisted of the sum of 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,3,4,6,7,8-HxCDF; and 1,2,3,7,8,9-HxCDF
- ***HpCDD/F*** which consisted of the sum of 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF;
- ***OCDD/F*** which consisted of the sum of OCDD and OCDF

For some data analyses and discussions, a toxic equivalent, or TEQ, concentration was generated. This procedure involves assigning individual toxicity equivalency factors (TEFs) to the seventeen 2,3,7,8 substituted CDD/F congeners (or to the subset of 17 which were measured in a given sample), then multiplying the concentration of individual congeners by their respective TEFs, and finally summing the products to get the TEQ concentration. As noted in Section 1, calculations of TEQ use the World Health Organization's Toxicity Equivalency Factor Scheme (Van den Berg et al., 1998). For compounds that were not detected, half of the detection limit was used in TEQ calculations and all other aggregations. Non-detects were mostly not an issue for this study; only the untreated pole and the tetra-chlorinated congeners of the freshly treated poles had a significant number of non-detects. A value of zero was used in TEQ calculations for compounds for which an interferant degraded the results.

5.2. Normalization

Because the dioxin concentrations in PCP formulations have changed over time and from batch-to-batch, and the technology for treating poles has

changed over time, it is impossible to know the initial concentration, or distribution, of dioxins in each pole. Therefore, raw concentration results needed to be normalized in some manner in order to compare results from different poles. Mean-normalized concentration ratios were calculated for each individual pole for this purpose. First, pole average concentrations were derived for each congener and aggregated group. These were developed by determining an average concentration for each of five radial locations defined as a function of the radial distance from the pole center: 0 (pole center); 0.3 *r*; 0.6 *r*; 0.8 *r*; and 0.9 *r*. The average radial location was most often derived as the average of four radial measurements — the center of the pole was measured only once, and sometimes there were only three measurements available for a radial location. The final pole average was then derived as the average of these five radial averages. A mean-normalized concentration ratio is the ratio of any observed congener or aggregated congener group concentration to the pole-average concentration for that congener/aggregated group for the pole from which the sample was extracted. A ratio greater than 1.0 means that the concentration for the point in question is higher than the pole average.

5.3. Contour plot generation

The contour plots were generated using MATLAB (Release 11, The Math Works). The contouring algorithm treats the data as regularly spaced polar grid points with each element connected to its nearest neighbors. The algorithm scans the data comparing the values of each block of four neighboring elements, a cell, to the contour level values. If a contour level falls within a cell, the algorithm performs a linear interpolation to locate the point at which the contour crosses the edges of the cell. The algorithm connects these points to produce a segment of a contour line. Fig. 3 illustrates the method used to determine the location of the contour boundaries in the contour plots. The plot area is divided into a polar grid. The values of the vertices of each cell within the grid are then examined to determine if a contour line will pass between them. In Fig. 3, the contour

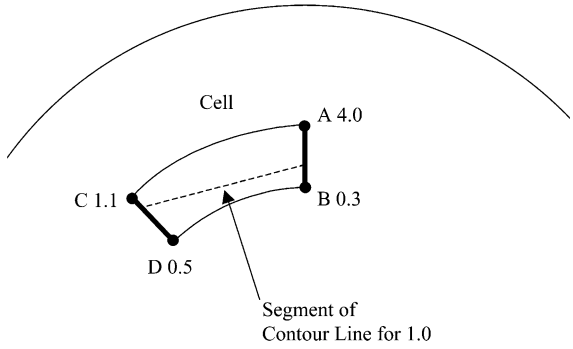

Fig. 3. Algorithm used to determine contour line locations.

line for the value 1 will pass through the segments between points A and B and points C and D. Once the segments of the cell that will be crossed by the contour line are identified, the location of the contour line segment is determined by interpolating between the values of the known points. The spacing of the grid elements is determined by the available data. In the raw data set, there are only four cells at each radial distance. Plotting these data directly would lead to skewed and uninformative depictions of the concentrations within the entire cross-sectional area. The size of the cells (as shown in Fig. 3) would be too large to be useful. To correct this situation, the size of the cells were reduced by interpolating between known points as shown in Fig. 4. Points A, B, C and D are measured values. The white points in Fig. 3 are interpolated from the known values. Three points per radial circumference within each sector were extrapolated in this manner. Also, and as indicated in Section 2, there were instances where less than four samples were obtained along a given radius. In sample locations where no measurement was made, concentrations were interpolated between the two measured samples along the radii surrounding the unmeasured sample. Figs. 5–9 show the final results of this exercise, showing concentration contours for the aggregated and normalized data of this study.

5.4. Results 1. Pole concentrations

Table 4 summarizes the observed average concentration of PCP and each dioxin and furan

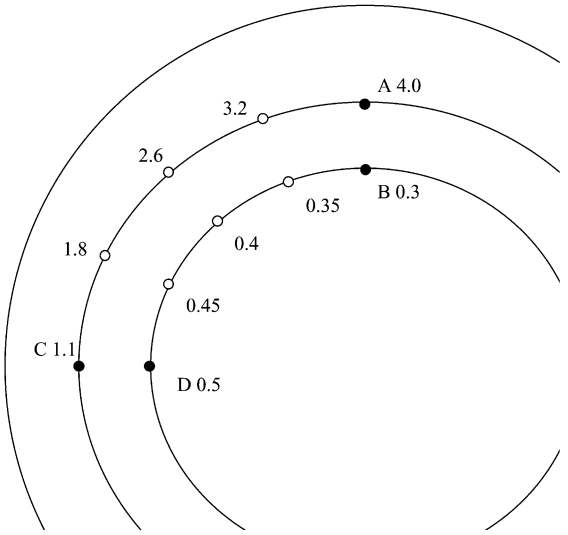

Fig. 4. Interpolation method used to create a useful grid size for contour generation.

congener, and aggregated group, in each of the poles (the procedure for deriving pole average concentrations was described above in Section 5.2). These averages do not capture the variation in concentrations in the four radial directions (N/S/E/W) within each pole or variation as a function of depth within a pole; such variations are described in more detail in sections below. These average concentrations are useful in understanding general trends over time in poles, and how dioxin in PCP-treated poles compares to dioxin in other environmental matrices.

The average concentrations in treated poles ranged over several orders of magnitude from a low value of 0.006 ng/g dry wood for the TCDD/F aggregate group to a high value of 9100 ng/g dry wood for the OCDD/F aggregate group and 48–7000 μg/g dry wood for PCP. The concentrations of PCP and the more highly chlorinated congeners were found to be reasonably consistent from the freshly treated through the 24-year-old pole, with a significant drop-off in the 34-year-old pole.

Table 4 suggests a change in 2,3,7,8-TCDD concentrations over time. The two fresh poles and the pole with 1 year of service had low concentrations, 0.008 ng/g (1 year), 0.006 ng/g (fresh) and ND (DL = 0.002 ng/g; fresh), whereas all other poles had measurable concentrations ranging from 0.02 to 0.08 ng/g. A similar trend is seen with 2,3,7,8-TCDF-lower concentrations were found in the 1-year-old and freshly treated poles as compared to all other poles. These profile trends are consistent with the changes in practices in the PCP industry to reduce the concentration of lower chlorinated CDD/Fs in technical PCP in recent years (EPA, 1999).

While Table 4 shows that the concentrations of the higher chlorinated congeners appear to be much lower in the 34-year-old pole, a closer examination of results from that pole show that there is a cluster of high concentrations of the hepta and octa CDD/F congeners in the outer portions of one of the four quadrants — the east quadrant. The concentrations of these congeners at the 0.9 *r* position in the east quadrant were over 10 times higher than the pole average, and the concentrations at the 0.8 *r* position were 3–5 times higher. The following shows how the pole average was affected, when including this hot spot (with HS) and not including it (*w/o* HS; results in ng/g dry wood):

	1234678-HpCDD	OCDD	1234678-HpCDF	1234789-HpCDF	OCDF
With HS	29	66	9.7	1.1	28
w/o HS	4	30	1.4	0.15	4.6

In addition to elevating the overall pole average, this hot spot affected the trend for this 34-year-old pole-the normalized concentration ratio for the outer part of the pole was very high. This will be discussed further below.

Fries et al. (1998) found similar CDD/F concentrations in PCP-treated wood in agricultural research facilities, as were found in the PCP-treated utility poles of this study. They collected and analyzed cattle confinement and housing wood samples from several agricultural research facilities around the US. This analysis of wood was prompted by unexpected high concentrations of CDD/Fs found in the cow's milk and adipose tissue in cows at these facilities. Numerous wood samples were taken, and the majority were found to contain PCP ranging in concentration from <10 μg/g

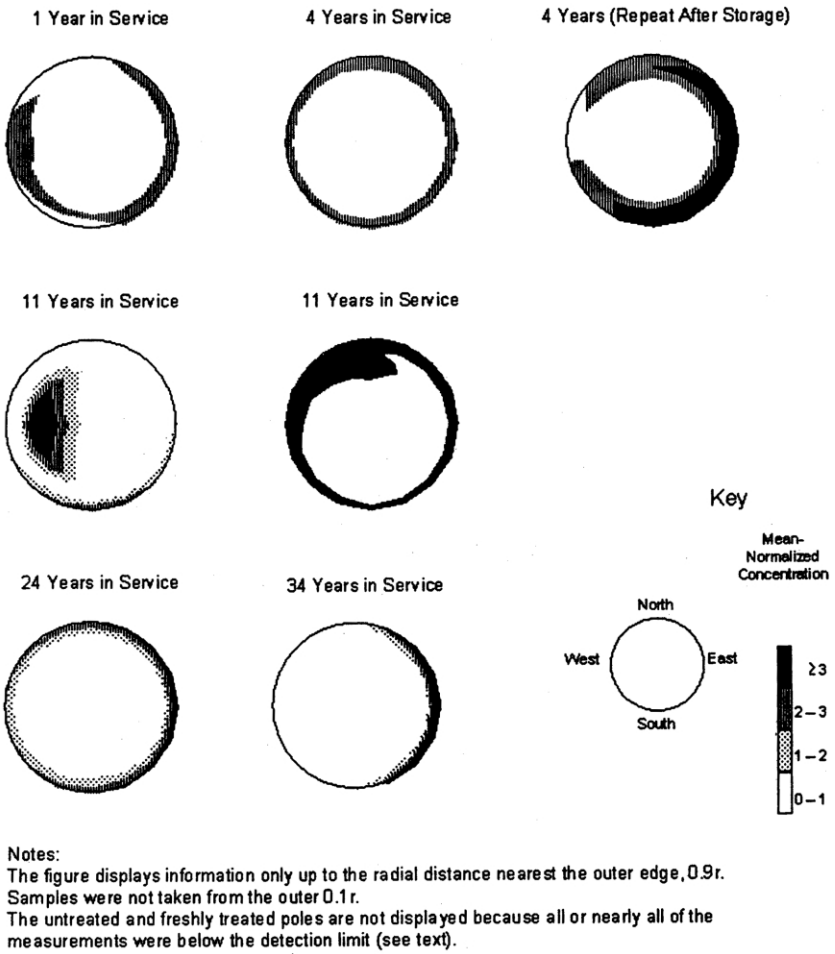

Fig. 5. TCDD/F normalized concentration ratio contours.

(ppm) to >5000 μg/g. Fries grouped his wood samples according to the levels of PCP found, from 'PCP not detected' (with detection limits of 0.5 μg/g) to 'PCP high' for samples with PCP concentrations ranging from 1580 to 8540 μg/g. The utility poles of this study had PCP concentrations >3000 μg/g (with the exception of the 34-year-old pole, which had a PCP concentration of 54 μg/g). For this study and that of Fries, concentrations of PCP in the hundreds to thousands of ppm (μg/g) are associated with dioxin TEQ concentrations in the ppb (ng/g) range, and OCDD/F concentrations in the hundreds to thousands of ppb range. 2,3,7,8-TCDD concentrations averaged 0.004 ppb for the two freshly treated utility poles of this study (one non-detected at 0.002 ppb detection limit and one detected at 0.0061 ppb), but were an order of magnitude higher in other treated wood, and even higher at a 1.2 ppb average in seven wood samples from Fries which had high PCP concentrations.

In general, the concentrations of CDD/Fs in the PCP-treated utility poles of this study and the PCP-treated wood described in Fries et al. (1998), greatly exceeds the CDD/F concentration in untreated wood and in soil and vegetation. This supports the concern that PCP-treated poles can be a reservoir source of dioxin-like compounds, as

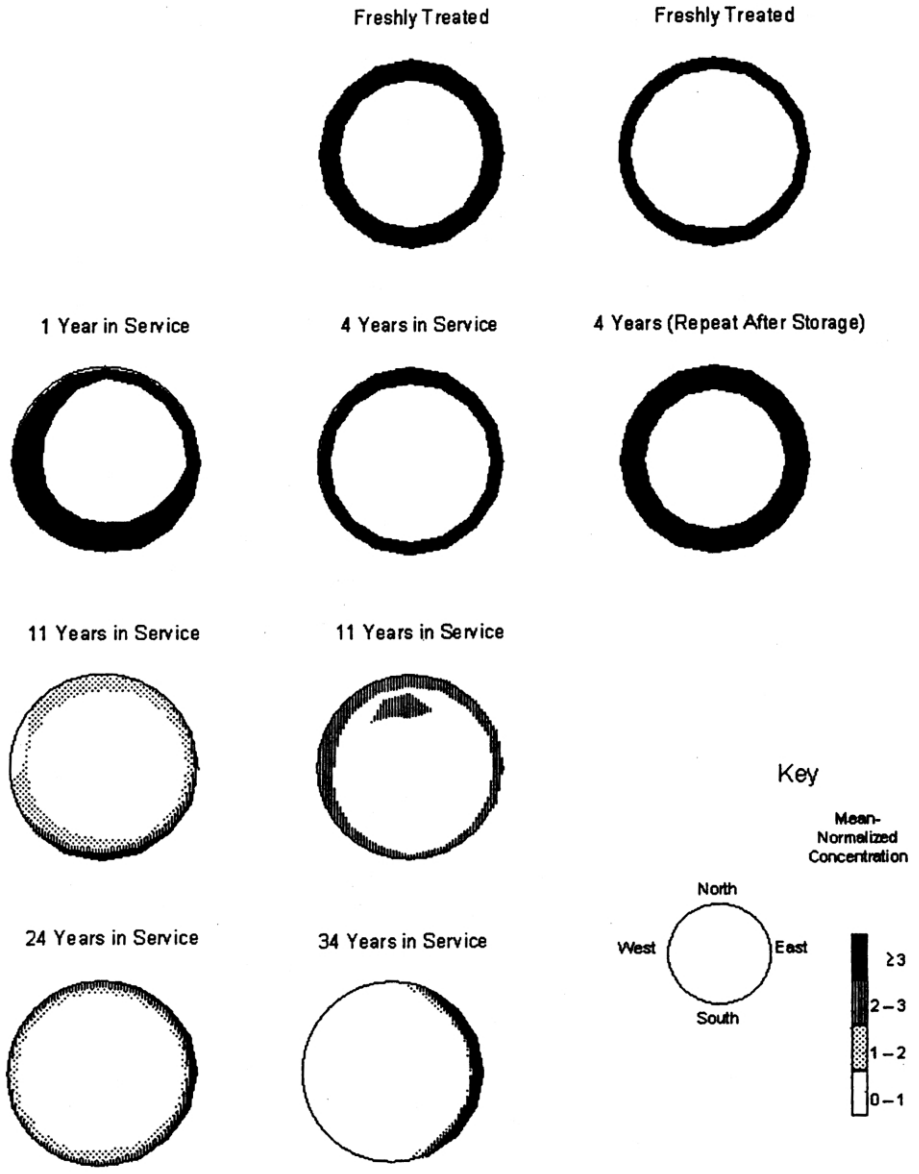

Fig. 6. PeCDD/F normalized concentration ratio contours.

discussed in the introduction. All of these treated wood dioxin concentrations are 3 to 6 orders of magnitude higher than concentrations of dioxins in soil and vegetation. While it is expected that most of this difference is due to the PCP in the wood, it is true that dioxins from the air are

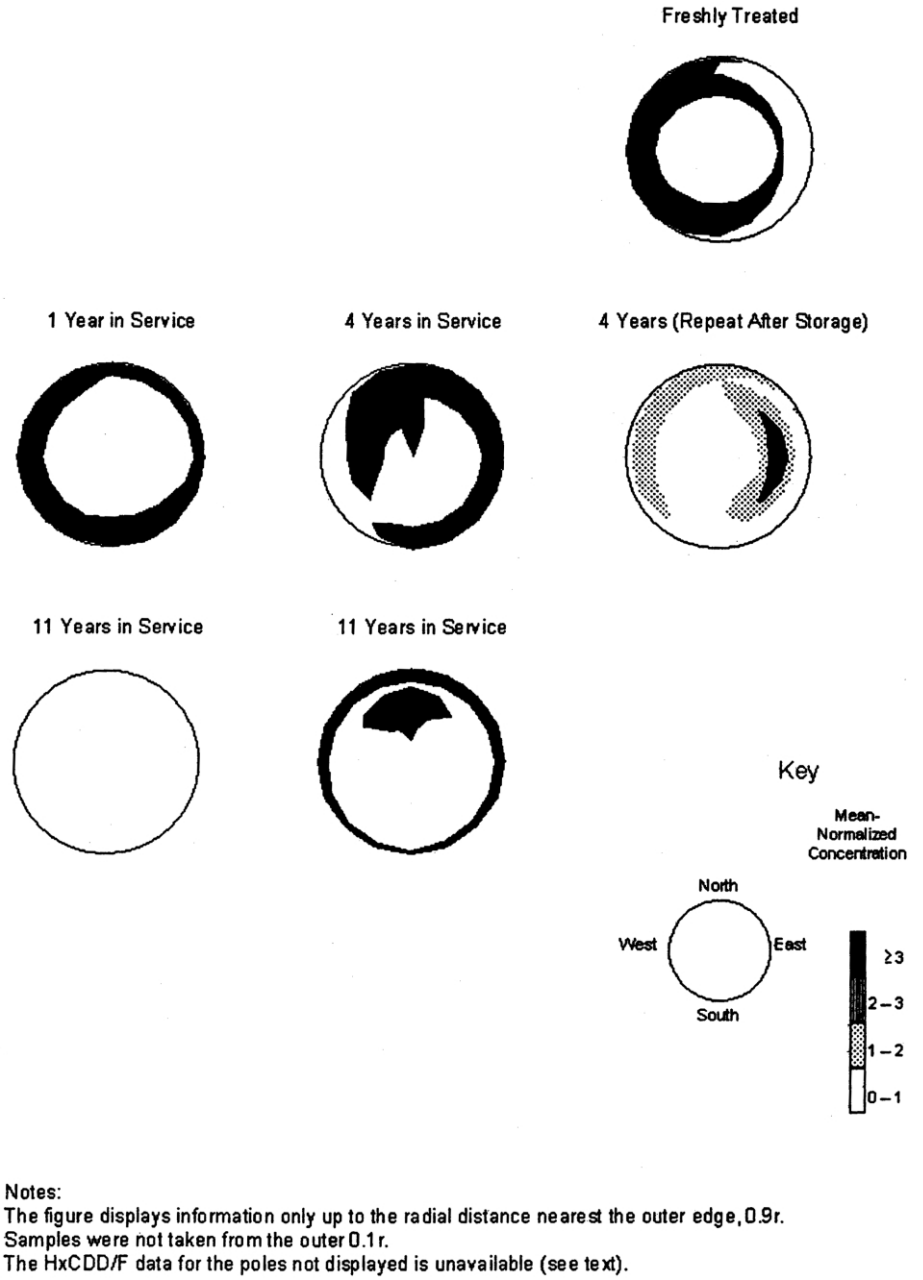

Fig. 7. HxCDD/F normalized concentration ratio contours.

absorbed into wood and that this could explain some of the elevation of dioxins found in the treated wood. However, if dioxins from the air would greatly impact standing wooden poles, they would also impact surface soils, and the environmental data do not bear this out. Typical concentrations of 2,3,7,8-TCDD in soil and hay in rural background settings are in the range of 0.0002 ppb

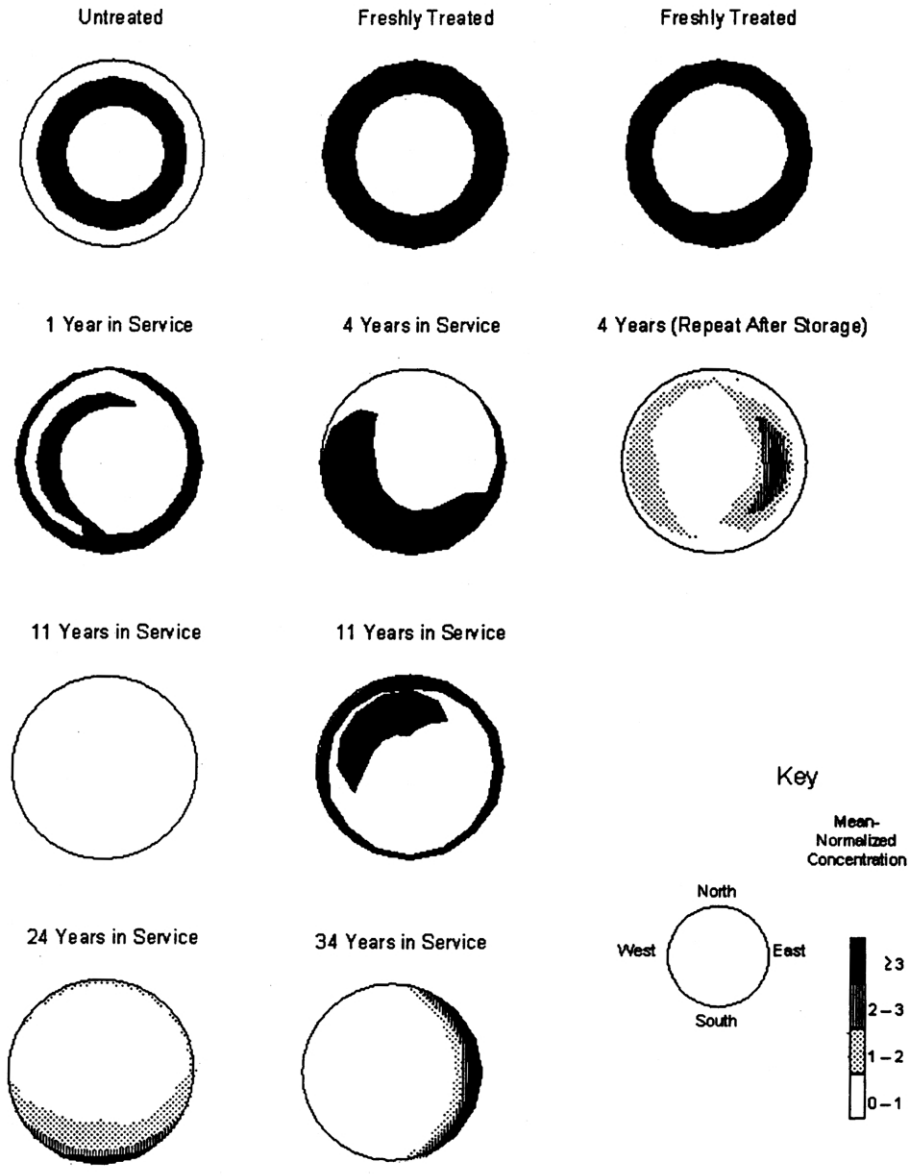

Fig. 8. HpCDD/F normalized concentration ratio contours.

(EPA, 2000b) and <0.0001 ppb dry wt. (Winters, et al., 2000), respectively, compared to findings described above for 2,3,7,8-TCDD in PCP-treated wood at >0.001 ppb up to 1.2 ppb. On a TEQ basis, rural soil and grass concentrations are in the range of 0.003 ppb and 0.0002 ppb dry wt. (EPA, 2000b; Winters, et al., 2000), compared to concentrations in the low ppb range in PCP-treated wood.

It is interesting to note that dioxin concentrations are higher in untreated wood from both studies,

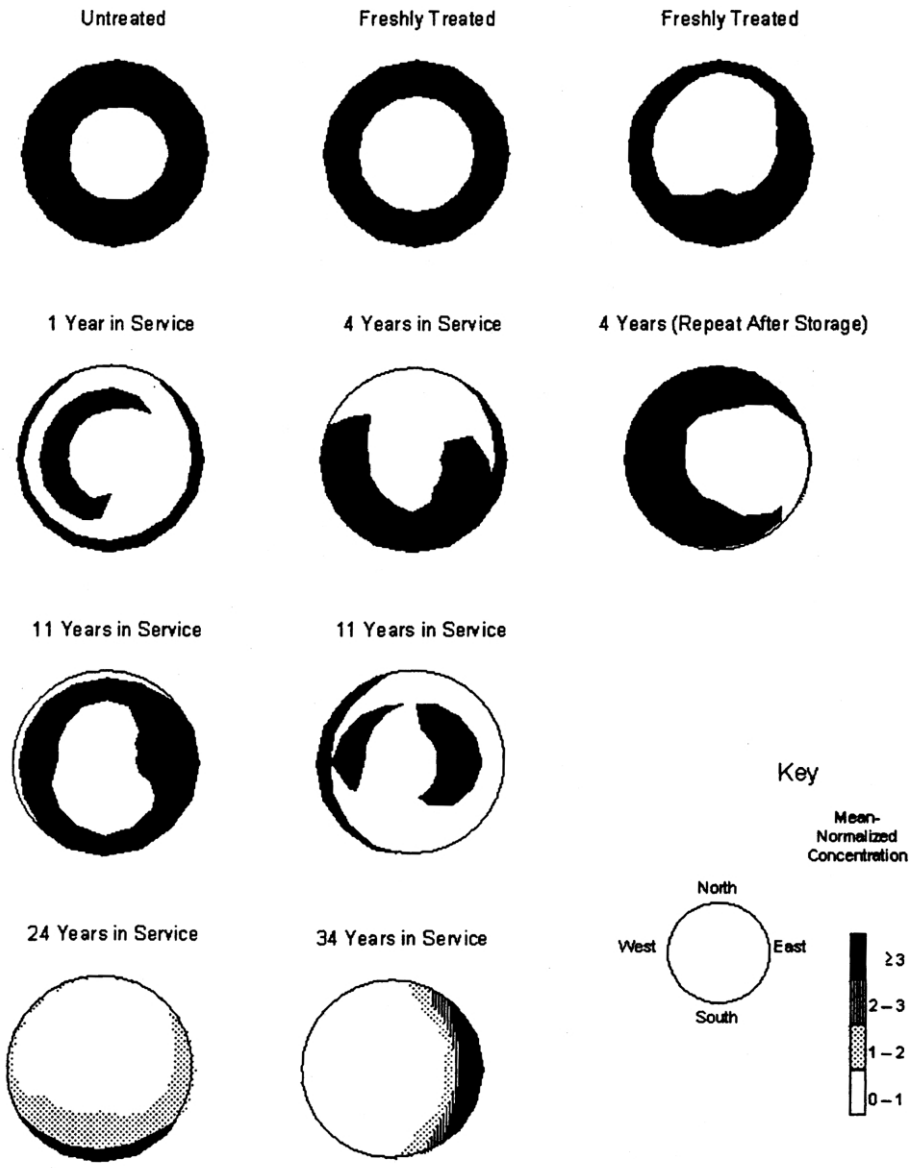

Fig. 9. OCDD/F normalized concentration ratio contours.

this one and the one by Fries, as compared to dioxins in hay and soil. The TEQ concentrations of 0.76 (this study, influenced by unusually high OCDD/F concentrations) and 0.02 (Fries study) ppb in the untreated wood compare to 0.003 ppb TEQ in soil and 0.0002 ppb TEQ in hay. Wood could have higher concentrations than hay simply because the wood is exposed to the atmosphere and depositing dioxins for much longer than hay, which is exposed only for a matter of weeks before

Table 4
Summary of observed average CDD/F and PCP concentrations

	Average concentration in sampled wood, ng/g dry wood									
Years in service	Untreated	Freshly treated	Freshly treated	1 year	4 years	4 years[a]	11 years	11 years	24 years	34 years
Year treated	–	1996	1999	1997	1994	1994	1987	1987	1973	1963
2,3,7,8-TCDD	ND[d] (0.0004)	ND[d] (0.002)	0.0061	0.008	0.022	0.023	0.079	0.026	0.059	0.020
2,3,7,8-TCDF	ND[d] (0.0005)	ND[d] (0.004)	ND[d] (0.028)	0.008	0.009	0.010	0.0055	0.019	0.0026	0.0009
Total TDCC/F	ND[d] (0.0009)	ND[d] (0.006)	0.0061	0.016	0.031	0.033	0.079	0.045	0.062	0.021
1,2,3,7,8-PeCDD	ND[d] (0.0006)	0.018	0.22	0.55	0.67	0.67	0.42	0.46	1.6	0.21
1,2,3,7,8-PeCDF	ND[d] (0.0005)	NA[b]	0.073	0.15	0.057	0.088	0.015	0.084	0.090	0.062
2,3,4,7,8-PeCDF	ND[d] (0.0004)	0.015	0.28	0.17	0.093	0.095	0.041	0.18	0.11	0.12
Total PeCDD/F	ND[d] (0.002)	0.33	0.57	0.87	0.82	0.86	0.47	0.72	1.7	0.40
1,2,3,4,7,8-HxCDD	NA[b]	NA[b]	1.8	3.4	2.2	5.5	0.8	1.4	NA[b]	NA[b]
1,2,3,6,7,8-HxCDD	NA[b]	NA[b]	4.9	12	26	28	9.6	12	NA[b]	NA[b]
1,2,3,7,8,9-HxCDD	NA[b]	NA[b]	1.2	6.4	9.5	6.1	1.4	2.0	NA[b]	NA[b]
1,2,3,4,7,8-HxCDF	NA[b]	NA[b]	1.4	5.6	8.8	4.4	3.2	4.0	NA[b]	NA[b]
1,2,3,6,7,8-HxCDF	NA[b]	NA[b]	1.7	2.6	1.1	2.1	0.30	0.59	NA[b]	NA[b]
2,3,4,6,7,8-HxCDF	NA[b]	NA[b]	2.2	4.7	3.0	2.8	1.4	1.7	NA[b]	NA[b]
1,2,3,7,8,9-HxCDF	NA[b]	NA[b]	4.9	0.78	0.92	5.7	0.30	0.79	NA[b]	NA[b]
Total HxCDD/F	NA[b]	NA[b]	18	36	52	54	17	23	NA[b]	NA[b]
1,2,3,4,6,7,8-HpCDD	67	200	330	870	700	840	320	1000	470	30
1,2,3,4,6,7,8-HpCDF	NA[b]	62	94	190	110	110	42	58	98	9.7
1,2,3,4,7,8,9-HpCDF	0.90	3.5	15	25	18	25	11	9.0	5.5	1.1
Total HpCDD/F	68	260	440	1200	830	980	370	1100	580	41
OCDD	680	2900	2700	6000	3600	3200	4500	4900	2300	66
OCDF	180	1200	1700	3100	1200	1300	800	410	650	28
Total OCDD/F	860	4100	4400	9100	4800	4500	5300	5300	3000	94
WHO-TEQ[c]	0.76	3.1	6.8	15	14	15	6.3	14	7.7	0.71
PCP (mg/g dry wood)	0.00012	7.0	3.1	NA[e]	NA[e]	4.1	NA[e]	NA[e]	4.4	0.048

[a] Repeat analysis of 4-year-old pole after storage for two years.

[b] Data for hexavalent congeners and a few other congeners from some poles were not usable due to diphenyl ether intereference or other reasons (see Section 6 above).

[c] Based on 1998 WHO TEF Scheme (Van den Berg et al., 1998). NA values are considered 0. Half the detection limited was used for undetected compounds.

[d] ND indicates that all concentrations for this congener in this pole were below the detection limit. The value shown in parentheses is the detection limit. One half of this value is used in calculating the TEQ.

[e] PCP values were not determined for some poles.

it is harvested. In comparison to soil, wood could be absorbing more atmospheric dioxins because it is higher in organic matter content.

5.5. Results 2. Replicability

The third objective of this study, as noted in the introduction, was to provide information from which the need for and design of a more exhaustive study can be assessed. An important determinant for the design of a larger study is the ability to replicate results — would poles of similar service times have similar results, and would additional samples representing the same location within even one sampled pole yield similar results? Three sets of measurements were made for the purpose of evaluating how well results can be replicated. One was a resampling of the 4-year-old pole after unsampled portions of it had been in storage for 2 years. The second was the sampling of two poles of the same age; these were the two 11-year-old poles. The third was a sampling of two freshly treated poles, though treated at different times and locations.

The analysis conducted to evaluate replicability is shown in Table 5. There, relative percent differences (RPDs) of sample pairs and of groupings of sample pairs, are displayed along with concentrations and the standard deviations (S.D.) of the RPDs. As described in the Analytical Methods and Quality Control section above, RPDs were generated for duplicate study samples as a QA/QC measure, and they are used here as a means to evaluate measurement variability. A complete set of results — those for all sample locations — are provided for 1,2,3,7,8-PCDD in Table 5. Average results over all sampling locations for a hexa, hepta and octa congener are also provided in Table 5.

For the QA/QC results shown in Table 3, the average RPD was 46% during the first round of sampling in 1998, and for the second round in 2000, the average RPD was 21%. The S.D. values around these average RPDs of 43 and 29 (rounds 1 and 2) also indicate variability around duplication of split samples — some were very similar (low RPD) and some were very different (high RPD). For the three tests of replicability described in this section, distinctly different samples were measured. A comparison of the RPDs and S.D. values of these paired samples with the QA/QC duplicate sample RPDs and S.D. values can provide an indication of whether differences in study samples were due to analytical variability or the two samples were truly different.

The three pairs are evaluated as follows.

5.5.1. Freshly treated poles

The two freshly treated poles, while sharing trends with depth as seen by higher concentrations at the outer portions (4 and 5 positions) as compared to inner portions (C, 2 and 3 positions), clearly had different concentrations. The RPDs were 144, 57 and 55, and the S.D. values around these RPDs were high at 35, 53 and 49. The high RPD of 144 for 1,2,3,7,8-PCDD reflects the difference in concentrations found — 18 ppt for the first pole and 220 ppt for the second pole. A similar discrepancy was found in the other toxic congener, 2,3,7,8-TCDD: it was non-detected in the first pole (DL = 2 ppt) while it was quantified at 6.1 ppt in the second pole. Other concentrations between the two poles were more nearly similar, but still the RPDs and S.D. values around the RPDs for these higher congeners are all higher than the QA/QC results. One can conclude that the variability seen is due to more than analytical variability, and that not all freshly treated poles can be considered ‘equal’.

5.5.2. Same 4-year-old pole

As seen in Table 4, a second sampling of the 4-year-old pole resulted in average pole concentrations very close to original concentrations. Most compounds were reanalyzed at concentrations within a factor of two of original analysis. The only exception was 1,2,3,7,8,9-HxCDF, found at 5.7 ppb during the second measurement after having been found at 0.92 ppb during the first measurement. The RPDs did show some variability, with average RPDs of 34, 48, 51 and 39. These RPDs appear to be slightly higher but still within the QA/QC RPDs, found at 46 and 21. The S.D. values around the RPDs were also low and comparable to the QA/QC S.D. values — they were 22, 26, 42 and 30 for the 4-year-old

Table 5
Summary of concentrations found (in ppt, dry wt.) and relative percent differences (RPDs,%) in paired poles used in replicability testing, including all results for 1,2,3,7,8-PCDD and summarized results for three other congeners

	Average concentration in sampled wood, pg/g dry wood and RPD (%)								
	Fresh poles			Same 4-year-old pole			Two 11-year-old poles		
Year sampled/RPD	1998	2000	RPD	1998	2000	RPD	1998	1998	RPD
Description	I. 12378-PCDD detailed results								
North N5	34	445	171	1560	1270	20	872	1320	37
N4	26	145	139	1050	1590	41	433	519	27
N3	15	61	120	207	261	23	60	281	163
N2	8	47	144	NA	69	–	NA	NA	–
C	2	300	198	143	116	21	200	83	125
South S2	8	65	156	74	72	3	177	81	2
S3	13	70	136	NA	215	–	NA	NA	–
S4	15	272	179	910	1550	52	547	1470	88
S5	40	625	176	1840	1860	1	2530	481	96
West W5	57	465	156	1970	941	71	173	706	156
W4	31	172	139	743	1190	46	330	1520	69
W3	13	97	153	379	510	29	316	748	13
W2	8	30	116	NA	56	–	NA	NA	–
C	5	NA	–	NA	NA	–	NA	NA	–
East E2	17	27	44	113	67	52	83	88	34
E3	14	56	119	NA	179	–	NA	NA	–
E4	24	101	122	849	1590	61	209	698	–
E5	31	479	176	2310	1800	25	1210	1570	34
	II. 12378-PCDD								
Pole mean	18	220	144	667	673	34	419	550	65
S.D. RPD			35			22			56
	III. 123678-HxCDD								
Pole mean	NA	NA	–	26340	27570	48	9560	12017	42
S.D. RPD						26			38
	IV. 1234678-HpCDD								
Pole mean	2.0E5	3.3E5	57	7.0E5	8.4E5	51	3.2E5	1.0E6	93
S.D. RPD			53			42			57
	V. OCDD								
Pole mean	2.9E6	2.7E6	55	3.6E6	2.3E6	39	4.5E6	4.9E6	45
S.D. RPD			49			30			39

Key: N5, North, position 5 outermost 0.9 radius; position 4 = 0.8 *r*; position 3 = 0.6 *r*, position 2 = 0.3 *r*; C = center. RPD, Relative Percent Difference = (high − low)/average × 100. NA, results not available due to non-detected or not analyzed.

pole replicate samples, while they were 43 and 29 for the QA/QC results. It can be concluded that the variability seen in the resampling of the 4-year-old pole at a different location a few years later showed results that were essentially the same as the original sampling — that differences could be explained by analytical variability.

5.5.3. Two 11-year-old poles

Like the two freshly treated poles, replicability was not found for the two 11-year-old poles. One pole's concentrations were consistently lower than the other pole's, within a factor of 5, with one exception — 2,3,7,8-TCDD. The concentration of this congener was three times higher in the generally lower pole. The RPDs for the four congeners were 65, 42, 93 and 45% — seemingly higher than the QA/QC finding of 46 and 21%. The S.D. values around the RPDs for the 11-year-old pairs at 56, 38, 57 and 39, appear outside the range of the 43 and 29 found for the QA/QC results.

In general, one would expect some variability between different poles in service due to the possibility of different wood types, different treat-

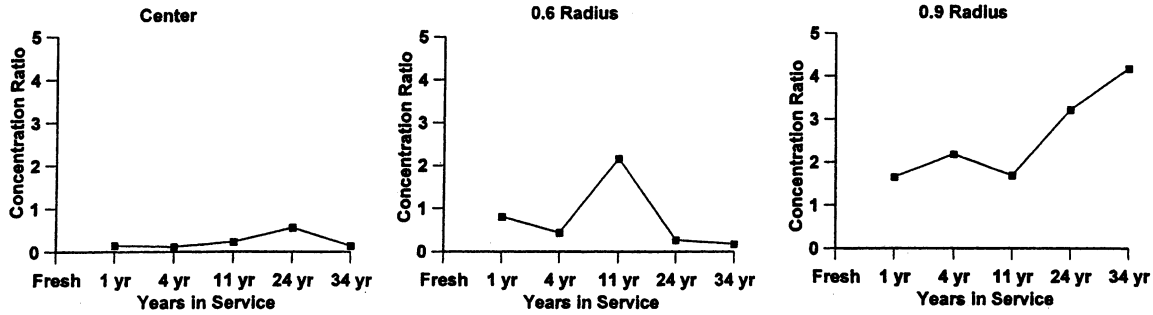

Fig. 10. The variation in the mean-normalized TCDD/F concentration with radial position and time in service.

ments, different PCP formulations, and different environmental influences. This was borne out in the replicability test for the 11-year-old poles. It was also found, a bit unexpectantly, that even two freshly treated poles of recent vintage had meaningfully different concentrations. With some assurance, it was found that while variability was found in sampling from two locations of the same pole, analyzed years apart, this variability appears to be within the variability of the analytical methods. Overall, these results suggest that if such a program were expanded, one could not necessarily rely on one pole to represent trends for one service time period.

5.6. Results 3. Concentration–depth profile trends

Figs. 5–9 illustrate the mean-normalized concentration ratio contours for each of the congeners groups examined. In Figs. 5–9, a ratio less than 1.0 shown as white space indicates that the concentration for that area is less than the overall pole average. Similarly, ratios greater than 1.0, shown as gradations of gray, mean that the identified area average concentration is greater than the pole average.

These figures illustrate observable pole-to-pole variation in distributions of normalized congener concentration ratios. Even in poles which have been in service for similar periods of time, such as the two poles that had been in service for 11 years, differences can be observed. A principle observation is that the ratios of all congeners in all poles tend to be highest in the outer regions of the pole and decrease towards the center. These figures show that the freshly treated poles have the most uniform concentration around the pole. As seen by the 24- and 34-year-old poles, over time the highest concentrations appear only on the outermost layer of the poles. This is a trend examined further in the next section.

Three additional important observations are also made from these figures:

1. The additional analysis of 4-year-old pole, which occurred 2-years after the first analysis, showed different concentration ratio/depth trends even though the average pole concentrations were similar (the section above on Concentration Results discusses and Table 3 displays the similar pole average concentrations). For example, in Fig. 5 showing the trend for the tetra congeners, the second analysis showed high relative concentrations in one half of pole, while the initial analysis showed relative uniformity after 4 years. This dissimilarity is continued for the other aggregate groups in Figs. 6–9. Two explanations can be offered for this trend: (a) congener levels could have changed over this 2 year time frame. This could have occurred by either a continuation of the original field processes which result in a redistribution of dioxins within a treated utility pole, or as a consequence of handling and sampling procedures in this study; or (b) The differences may have little to do with passage of time, but reflect the fact that sampling occurred in the two different locations within the same pole and may reflect spatial variability.
2. The ‘hot spot’ for the hepta and octa congeners for the 34-year-old pole is shown in Figs. 8 and 9. Except for that one hot spot point, all the

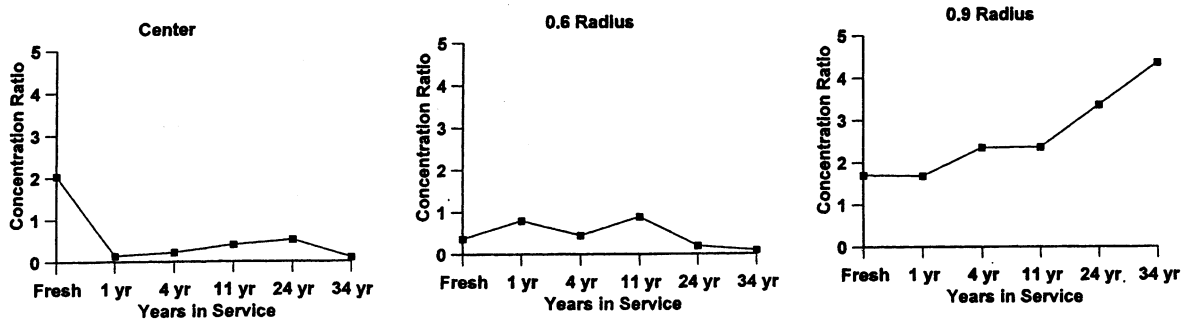

Fig. 11. The variation in the mean-normalized PeCDD/F concentration with radial position and time in service.

area shows a concentration ratio less than 1.0.

3. Perhaps the most meaningful observation that can be made from these figures is that both freshly treated poles appear to have uniform concentrations of CDD/Fs to at least the first two sampled depths of 0.9 *r* and 0.8 *r*, and in all pole quadrants. Over time, even after 1 year, the concentration–depth profiles are no longer as uniform. They are not even uniform among aggregate groups with the same pole. For example, for the second 4-year-old pole sample, the tetra through hepta aggregate groups are relatively elevated on the east side of the pole, whereas the octa aggregate group is relatively elevated on the west side of the pole. Two explanations can be offered for this overall observation-CDD/Fs in poles in service degrade at varying rates leading to this non-uniformity, or CDD/Fs in poles in service migrate within poles over time. The next section on concentration–depth profile trends evaluates this second possibility in more depth.

5.7. Results 4. Concentration–depth profile trends over time

Figs. 10–14 illustrate the variation in concentration ratios with radial location and age for each of the aggregate groups examined. Each figure is specific to an aggregate group and a radial location. The figures are in groups of three, with results displayed for the pole center, for 0.6 *r* (approx. the midpoint of the pole), and 0.9 *r* (the outermost area sampled near the outside edge of the pole). For each of these radial locations, the concentration ratios found in each of the four quadrants sampled (or subset of the E/W/N/S quadrants sampled) were averaged. Also, the corresponding ratios obtained from the two freshly treated, the two 4-year-old, and the two 11-year-

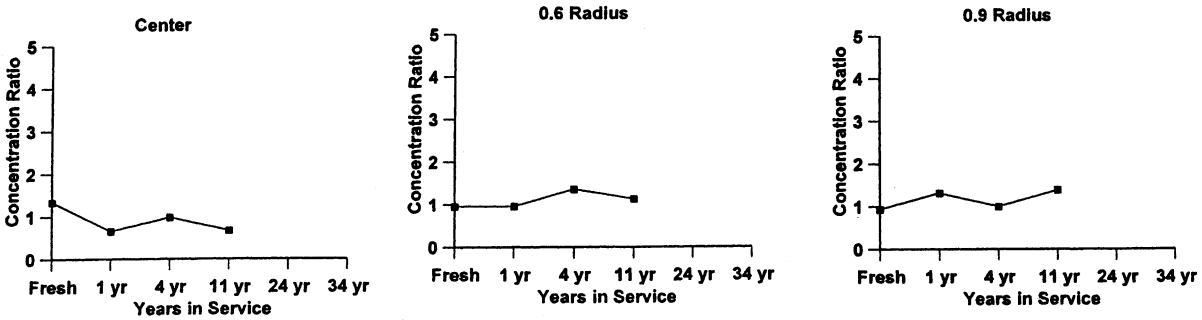

Fig. 12. The variation in the mean-normalized HxCDD/F concentration with radial position and time in service.

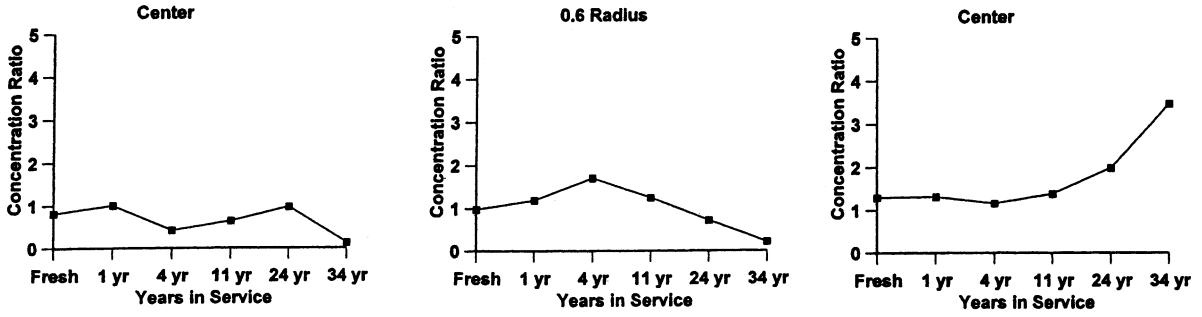

Fig. 13. The variation in the mean-normalized HpCDD/F concentration with radial position and time in service.

old poles were averaged to provide single data points for each period of service.

With few exceptions, the normalized concentration ratios of all aggregate groups are higher in the outer portions of the poles than in the inner portions. As seen in Figs. 10–14, the ratios are nearly always greater than 1.0 for the 0.9 *r* position, ranging as high as 4.0, while for the center and 0.6 position, the ratios are nearly always near to or less than 1.0. There also appears to be changes in these ratios over time-as the pole age increases, the ratios at the 0.9 *r* position increases, and similarly, ratios for the center and 0.6 *r* positions decrease. This temporal increase at the 0.9 *r* position is most pronounced for the TCDD/F and PeCDD/F aggregate groups. There, the ratios for the 24 and 34-year-old poles exceed 3.0.

The relationship between location and concentration becomes less marked, but still present, for the more highly chlorinated congeners. However, as described earlier, the 34-year-old pole had the 'hot spot' for hepta and octa congeners, particularly for the furan congeners. Shown in Fig. 15 are the 0.9 *r* location results for OCDD and OCDF separately. It is seen there that the OCDD results for the 34-year-old pole were similar to 24-year-old, while there was a large relative jump from the 24- to the 34-year-old pole for the OCDF congener.

One other important trend can be seen in these figures. There appears to be a slight rise in ratios for all aggregate groups in the center position for the 24-year-old pole. This trend appears to be related to moisture content. The highest moisture content for all poles and sampling locations occurred at the center position of the 24-year-old pole. The moisture content of the center of the 24-year-old pole averaged 54% (for two samples taken), while the average of all other moisture content measurements in that pole was 20% ($n=16$). All other poles had moisture contents near to and less than 20%. This 24-year-old pole also had a very high PCP concentration in the pole center, it was 9.4 mg/g (parts per thousand), while it

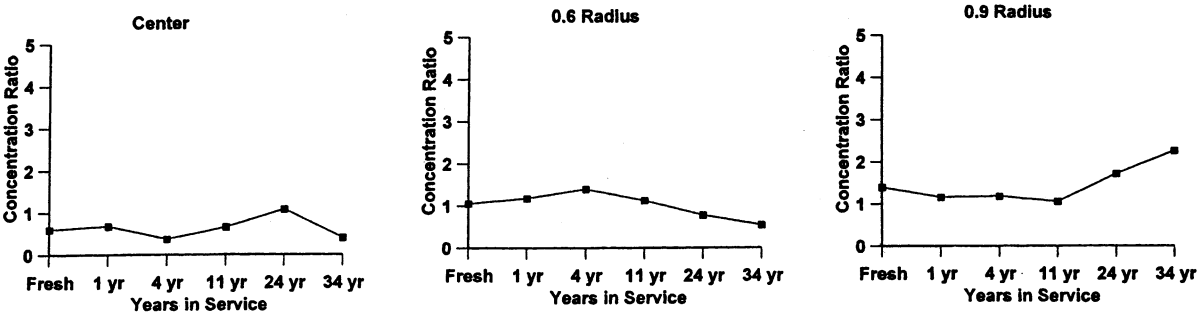

Fig. 14. The variation in the mean-normalized OCDD/F concentration with radial position and time in service.

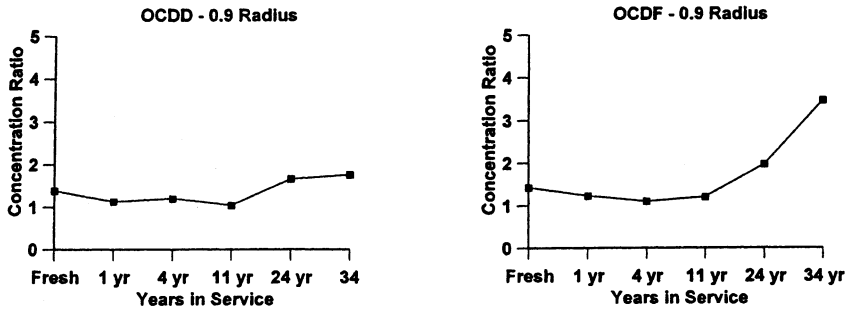

Fig. 15. The variation in the outer radial position, 0.9 *r*, for the two octa congeners, OCDD and OCDF.

averaged 3.1 mg/g for all other samples ($n=16$), and 5.3 mg/g for the outer edge samples only ($n=4$). This suggests that there was migration of PCP and CDD/F residues in this 24-year-old pole, not only to the outer portion of the pole, but also to the pole center, which may have been associated with high within-pole moisture content.

6. Discussions and conclusions

While it is difficult to extract meaningful conclusions from small, multidimensional data sets such as the one generated in this study, a few significant observations can be made:

1. Average CDD/F and TEQ concentrations in PCP-treated wood were very much higher, in the range of 2–6 orders of magnitude higher, than soil and leafy vegetation concentrations. This underscores the importance of utility poles as a reservoir source for dioxins. The presence of high concentrations and the ability to measure them also addresses the first objective of this study — to develop a reliable method for measuring spatial distributions of dioxins in treated poles.
2. Older poles had quantifiable concentrations of 2,3,7,8-TCDD, ranging from 0.02 to 0.08 ng/g (treated in 1994 and earlier), while more recently treated poles had lower concentrations at ND (DL = 0.002 ng/g), 0.006 and 0.008 ng/g (treated in 1996, 1999 and 1997, respectively).
3. Meaningful variability in concentrations was found in limited tests for replicability. These tests include the sampling of poles with similar service times (two freshly treated poles and two 11-year-old poles) and a second full sampling of the same pole (sampling at a different location on the same pole). The variability found in the second sampling of the same pole is similar to the variability found in the analytical chemistry QA replicate sampling, while the variability found for the two sets of different pole (11-year-old and freshly treated poles) suggest that other factors contribute to the variability, i.e. different PCP formulations, different environmental influences. This suggests that an expanded program should strive to sample as many poles as possible.
4. Current PCP treatment appears to result in uniform distribution of dioxins around the pole to a meaningful depth into a utility pole — at least until the 0.8 *r* location that was measured in this study. However, over time, even a short amount of time such as a few years, concentrations are no longer uniform around the pole and with depth.
5. CDD/F relative concentrations, as evaluated using concentration ratios, are consistently higher in the outer portions of the poles than in the middle and center of poles. This trend tends to be most marked in older poles and for the lower chlorinated congeners; that is, most of the CDD/F compounds tended to appear in outer portions of older poles as compared to younger poles.

There are several possible explanations for these last two trends:

- The treatment processes for older poles (i.e.

24–34-year-old poles) may have been less efficient than those currently used. The distribution observed in these older poles may simply reflect the original distribution of CDD/Fs in the pole.
- CDD/F may have degraded at a greater and non-uniform rate in the inner portions of the poles than in the outer portions.
- There may have been migration of CDD/Fs within the pole, possibly towards the outer part of the pole over time.

Of these three possibilities, the second seems most unlikely due to known patterns of dioxin degradation: degradation is extremely slow particularly when the compounds are sorbed to organic matter such as wood, and degradation is generally photolytic for lower chlorinated congeners (EPA, 2000b). The first explanation may have some truth. This first explanation would not explain, however, why there is concentration variability in 1- and 4-year-old poles (i.e. recently treated) that is not seen in freshly treated poles. It could be argued that the concentration profiles are most consistent with the third mechanism. The lower chlorinated congeners appear to have the most marked temporal trend, although even the HpCDD/F OCDD/F aggregate groups also appear most in the outer portions of older poles.

If dioxin migration were occurring to outer portions of PCP-treated utility poles, then a possible transport mechanism could be convective transport. The wood treatment process involves forcing the PCP preservative under pressure into the poles. Thus initially, the outer surface to some distance into the pole is saturated with the preservative fluid. After treatment, the forces of pressure and gravity will cause the fluids to slowly move through cracks and pores. The direction of this movement will depend on the geometry of the cracks, but is likely to favor movement toward the outside since cracks in wood tend to open up in this direction. As noted in the introduction, seepage of preservative oils on the outer surface of poles have been observed. Such seepage is likely to be enhanced in the summer when the higher temperatures reduce the viscosity of the fluid and expand the fluids increasing the pressure within pores and cracks. The dioxins dissolved in the preservative fluids will be carried with it. After a period of time, the degree of saturation will decline and convective flow will eventually cease.

The dioxins in treated wood could also move by molecular diffusion. As evaporation occurs at the outer surface a concentration gradient is established that would encourage dioxin molecules to diffuse outwards. Some diffusion may also occur toward the center of the pole where concentrations are low due to lack of penetration during the initial treatment. This process could occur in a liquid phase in the saturated wood pores or in a vapor phase in the unsaturated portions. Since the lower chlorinated dioxins have a higher vapor pressure than the higher chlorinated dioxins, they would dominate any vapor phase diffusion. This process is also likely to decline over time as concentrations gradients decline.

The above discussion explains two mechanisms by which dioxins could migrate within poles. The cross sectional distributions suggest this migration has occurred primarily via convection rather than diffusion. This is based on the assumption that if diffusion dominated, the cross-sectional profile would flatten over time as the dioxins move away from areas of peak concentration. Figs. 10–15, however, suggest that the pattern of high levels on the outside and low levels on the inside persist over time and in fact may become more pronounced, i.e. levels in the center decrease and levels on the outside increase. This trend suggests that dioxins migrate toward the outside of the pole, but the question remains how much of the dioxins are released from the pole. Such releases could occur by the following mechanisms:

- Evaporation: Although dioxins have low volatility, the lower chlorinated compounds have been shown to partition about equally between solid and vapor phases in the atmosphere under equilibrium conditions.
- Seepage: As discussed above, the flow of carrier fluids within the poles appears to account for most of the dioxin movement within the pole. These fluids have been observed to seep from poles and may carry dioxins with it. Elevations of dioxins in soils near treated poles have been observed. Precipitation events could enhance

export of oils and associated dioxins from the pole surface.

- Degradation: Dioxins at the very edge of the pole may be exposed to sunlight and degrade via photolysis or photooxidation. Although dioxins are relatively stable in the environment, experiments have shown that they can degrade slowly via these processes.
- Vapor diffusion: In older poles where edges are dry, the dioxins may reach the edge via vapor phase diffusion and continue to diffuse out into the atmosphere.

Since all of these mechanisms are physically plausible, it seems likely that at least some environmental releases are occurring.

Ultimately, though, a definite conclusion that dioxins are being released, and even more so, the size of a potential dioxin release, cannot be made with the data in this study because of these uncertainties: (1) it was impossible to know the concentrations and total mass of dioxins in the aged poles at the time when they were initially treated due to the lack of appropriate records. Although this study included an analysis of freshly treated poles, the data for these poles cannot be assumed to be representative of initial conditions in older poles due to changes in industry practices; and (2) fairly large spatial variability was observed in dioxin concentrations within a pole. This makes it difficult to know how representative a set of samples are and ultimately how to accurately calculate total mass of dioxin present in aged poles. These two problems prevented making mass balance calculations, which would be necessary to ascertain a potential amount released over time.

This was an exploratory study to evaluate if a relatively inexpensive, one-time, wood sampling program could provide insight on the fate of dioxins in treated utility poles. As discussed above, the project did yield some useful insights on the nature and magnitude of migration within the pole, but could not provide release estimates. This experience suggests that a more robust approach would be better in future attempts to empirically measure dioxin releases from utility poles in real world settings. A field study that involves sampling several freshly treated poles and then repeatedly sampling each pole over a long time period (i.e. 5 years or more) could yield more definitive data regarding the fate of dioxin in PCP-treated utility poles. At each sampling time, multiple samples over different heights and depths would be needed to ensure a representative sample. Ideally the poles would be made of different wood types and would located in different regions, to capture these potentially important confounders. Obviously this would be an expensive and time-consuming program but it appears to be the best way to obtain reliable estimates of dioxin releases from utility poles.

7. Disclaimer

The views expressed in this article are those of the authors and do not necessarily reflect the view or policies of US Government Agencies.

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